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Absorption of carbon dioxide in aqueous ammonia

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Abstract

Aqueous ammonia can be used to capture CO₂ from flue gas of coal-fired power plant with quick reaction rate, high removal efficiency, and high loading capacity of CO₂. It is thought to be a promising technology. However, the CO₂ absorption rate, diffusion rate and VLE (Vapor liquid equilibrium) in aqueous ammonia have still been rarely researched. More research is necessary for these characters of ammonia solution as CO₂ absorbent. The paper will focus on the fundamental characteristics of CO₂ in aqueous ammonia.

A series of tests were conducted in a semi-batch reactor that has been developed in this paper. CO₂ removal efficiencies at different concentrations of aqueous ammonia have been studied in the similar operation conditions to compare their basic characters in the CO₂ absorption process. And a small wetted wall column (WWC) with a contact area of about 41.45 cm² was also built for the study of the absorption rate, diffusion, and solubility of carbon dioxide in the aqueous solution. In the paper, reaction rate and overall gas transfer coefficient were studied. The concentration of ammonia ranges from 1, 5, 10 to 15. CO₂ and N₂ are used to simulate the flue gas. The concentration of CO₂ ranges from 5, 10, 15, to 20%. The reaction temperatures are 20 °C and 40°C. It is indicated in this paper that the best concentration of aqueous ammonia should be selected from 5% to 10%. And aqueous ammonia has a high *Flux* in WWC, which is three times higher than that of MDEA+ PZ, under the same condition. It is also found that *K_G* is appropriate to be used in the mass transfer process of the carbon dioxide absorption by aqueous ammonia. All of these experiments established foundation for the further study of CO₂ removal by ammonia.

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Keywords: Carbon dioxide; Removal efficiency; Aqueous ammonia; Absorption rate; Mass transfer

1. Introduction

Carbon dioxide is the major greenhouse gas in the world that needs to be reduced. There are various technologies used to separate CO₂ from flue gas. These include chemical solvent methods, physical absorption methods, cryogenic methods, membrane systems, biological fixation, and the O₂/CO₂ combustion process.

Compared with the chemical plant, power plant has a large flue gas flow, different ingredients, relatively low CO₂ concentration and other characteristics. So the chemical solvent methods are generally recognized as the most effective technologies at present. This requires that the researchers developed a relatively low-cost, low-energy requirement CO₂ capture technology.

Among the conventional CO₂ chemical removal processes, the monoethanolamine (MEA) process has been comprehensively studied and successfully used in chemical plants for CO₂ recovery. Although the MEA process is a promising system for the control of CO₂ emissions from massive discharging plants, it is an expensive option since the cost of CO₂ separation may range from US\$40 to 70/ton of CO₂ removed^[1](Chakma (1995)). In addition, it has several major problems including a slow absorption rate, a small solvent capacity, etc^[2]. (Molburg et al. (1994)).

Previous research shows that aqueous ammonia have a higher absorption capacity than that of monoethanolamine (MEA) at same temperatures and pressures. The CO₂ removal efficiency of aqueous ammonia can reach 95~99%, even 100%, and MEA is

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generally 90%^[3], An absorption capacity of aqueous ammonia can be higher than 1.0kgCO₂/kg solvent, and MEA is only 0.36kg CO₂/kg MEA^[4].

A series of tests was conducted in a semi-batch reactor that has been developed in this paper. CO₂ removal efficiencies of aqueous ammonia have been studied. And a small wetted wall column (WWC) was also built for the study of the absorption rate, diffusion rate, and solubility of carbon dioxide in solutions.

2. Experimental apparatus and methods

2.1 semi-batch reactor

First of all, a semi-batch reactor has been used in this paper. The factors influencing CO₂ removal efficiency in CO₂ loading process has been got in this paper, this is aqueous ammonia concentration. And the ammonia solution have been compared in the similar condition to study their basic characters as loading solution in CO₂ loading process, this established foundation for the further study of CO₂ loading by aqueous ammonia.

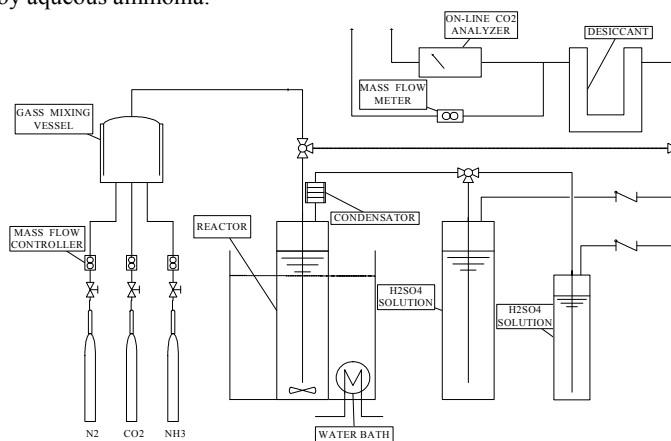


Fig.1. The experiment system of the semi-batch reactor

However many results have been got by semi-batch reactor so far, the principle of the absorption process such as the CO₂ absorption rate, diffusion rate and VLE (Vapor liquid equilibrium) in aqueous ammonia have still been rarely researched. For this reason, a small wetted wall column (WWC) with a contact area of about 41.45 cm² has been built for the study. This paper focuses on the relevant work of the reactor construction and the system commissioning, and a preliminary measurement of aqueous ammonia and carbon dioxide apparent reaction rate and mass transfer coefficient were also introduced.

These works laid an important foundation for the further study of the aqueous ammonia removal of carbon dioxide removal by aqueous ammonia.

2.2 The wetted-wall column

Mshewa, M. M. (1995) in Austin first built and used a wetted-wall column (WWC), which can hold a pressure from 1 to 8 atm to test the carbon dioxide desorption/absorption with aqueous mixtures of methyldiethanolamine (MDEA) and diethanolamine (DEA)^[5]. Then a lot of researches have been done on the amines in the same apparatus by Gary.T Rsochelle et al.

There are also some researchers from India^[6] (India Institute of Technology), Taiwan^[7] (Chung Yuan Christian University) and Korea^[8] (Yonsei University) used their WWC to do many experiments to study the carbon dioxide desorption/absorption with a variety of amines.

A wetted wall column with a contact area of about 41.45 cm² has been built in this paper at The Department of Thermal Engineering in Tsinghua University in China, and the details shows in Fig.2.

The main reactor of the wetted-wall column, depicted in Fig.2, was used as the gas-liquid contactor throughout the equilibrium and rate experiments. The contactor was constructed from a stainless steel tube with a well-defined surface area (41.45 cm²) and a characteristic liquid film mass transfer coefficient similar to that of a packed tower. The stainless steel wetted-wall, measuring 11.0 cm in height and 1.2 cm in diameter, is a tube extending from the liquid feed line into the column housing. The gas-liquid contact region is enclosed by a 31.0 cm thick-walled glass tube, separating it from a water-bath.

According to the problems of the past wetted-wall column, many of the new design have been used to improve the structure of the reactor. Firstly, Fluent Software is used to simulate the gas flow inside the reactor to find the best way for the inlet gas diffusion. A baffle-board is welded at the gas inlet to change the direction of the gas flow and make the liquid film not be disturbed. This change has been proved by a series of experiments to be necessary. Secondly, to solve the problem of the outlet liquid accumulated at the bottom of the column, a swallow-tailed groove on the bases of the reactor was processed. This can make the gas inlet and the liquid outlet to be completely separated and be non-interfering.

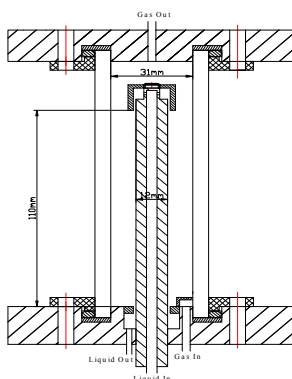


Fig.2. Schematic of the wetted-wall column

2.2 The experiment system

The chemical solution of interest is pumped through the inside of the tube, overflows, and is evenly distributed across the outer surface of the tube. After collection at the base of the column, the liquid is pumped back to a liquid reservoir. Gas enters near the base of the column, counter-currently contacting the liquid as it flows up into the gas outlet.

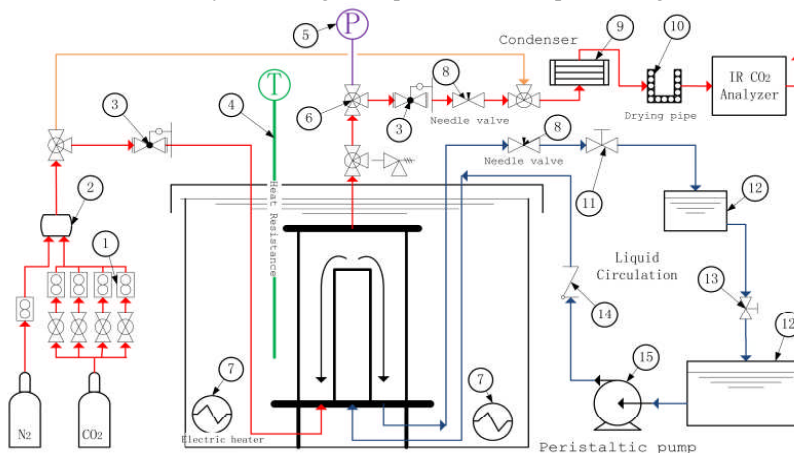


Fig.3. Overall experimental flowsheet of the wetted-wall column

The water/oil-bath, with circulation of the water/oil inside, is used to control the temperature of the inlet gas, liquid and the reactor. Two reservoirs are used in this system, one of them is used for the amine solution storage, and another one is used to holdup the waste solution out of the reactor. A Cole-Parmer micro-pump pushes the solution from the reservoir through a coil submerged in the water/oil-bath, flowing through a rotameter for flowrate determination. The liquid flow rate was 2–3 cm³/s. After heating, the solution flows into the wetted-wall column. After contacting the gas stream, the solvent returns to the reservoir.

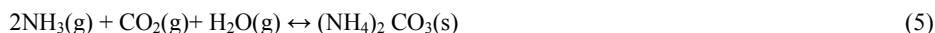
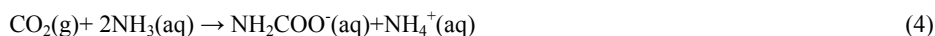
The total pressure used in this work was around 1 to 2 atm. To minimize gas film resistance, the gas flow rate was approximately 4.5 to 5.5 SLPM. A 10 SLPM mass flow controller is used to meter nitrogen flow. The carbon dioxide flowrate is metered with a 1 SLPM mass flow controller in this paper. Other 3 mass flow controllers of CO₂ are 0–5ml, 0–50ml and 0–0.2SLPM. All the valves in the gas-line are used to adjust the pressure in the reactor from 1 to 100Psi. The metered gases were mixed prior to entering the wetted-wall column. After exiting the contactor, excess water was removed by passing the stream through a condenser. A drying column filled with Silica was used to remove the remaining moisture. A carbon dioxide analyzer was used to measure the CO₂ concentration of the dry gas with infrared spectroscopy.

3. Theory

3.1 Theory of NH₃-CO₂ Reactions

Possible reactions between ammonia and CO₂ are as following [9–13] (Brooks and Audrieth (1946), Brooks (1953), Hatch and Pigford (1962), Shale et al. (1971), Koutinas et al. (1983)):





The above reactions proceed at various temperatures and operation conditions. Ammonium carbamate ($\text{NH}_2\text{COONH}_4$) is formed by the reaction of carbon dioxide and ammonia in the dry condition under room temperature and a pressure of 1 atm. It is very soluble in water; therefore, under moist air the hydration product of ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) is produced under room temperature^[9] (Brooks and Audrieth (1946)).

At room temperature and atmospheric pressure, reaction equations (4)–(8) also possibly occur. The formation of ammonium (NH_4^+) and carbamate (NH_2COO^-) ions is very fast, and reaction equation (4) is irreversible^[11] (Hatch and Pigford (1962)), and the reaction equations (5)–(8) are reversible^[10,12] (Brooks (1953), Shale et al. (1971)).

The explosive limit for NH_3 gas is 15–28% (v/v)^[14] (Merck (1996)). Therefore, in order to be safety and simplicity, the wet method is used in this study. Reaction equations (7) and (8) are the most probable in this study for CO_2 removal by aqueous ammonia scrubbing.

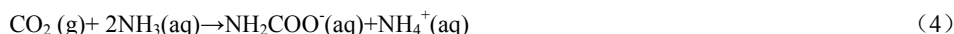
3.2 aqueous Ammonia and CO_2 Reactions

The total reaction of aqueous ammonia absorb carbon dioxide can be described as the equation (9):

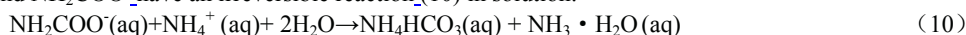


The actual process of the reaction is more complicated, that can be described as step-by-step reactions.

First of all, the (4) equation (described in 3.1) occur, and CO_2 and NH_3 react to generate $\text{NH}_2\text{COONH}_4$, then $\text{NH}_2\text{COONH}_4$ hydrolyzes in solution instantaneous.



Then, NH_4^+ and NH_2COO^- have an irreversible reaction (10) in solution:



At the same time, the complex balances of solute ionizing and ion reactions are happening in the solution, and the reaction equations are (11)–(15) as follows:



4. Experimental Section

4.1 CO_2 removal efficiency

Bai (1997) indicate a high potential of CO_2 scrubbing with a fast absorption rate by the 28% aqueous ammonia^[4]. The CO_2 removal efficiency may be higher than that by the conventional MEA process (90%) under proper operation conditions.

James T. Yeh et al (NETL, 2005) found in the experimental system, the kinetics was the most important factor to control the reaction, and another factor was the impact of the gas-liquid contact. James T. Yeh also indicated that a high concentration of

ammonia should be used. To consider the practical issues such as ammonia volatilization, however, the appropriate concentration must be selected. And a low-temperature reaction was also recommended^[15].

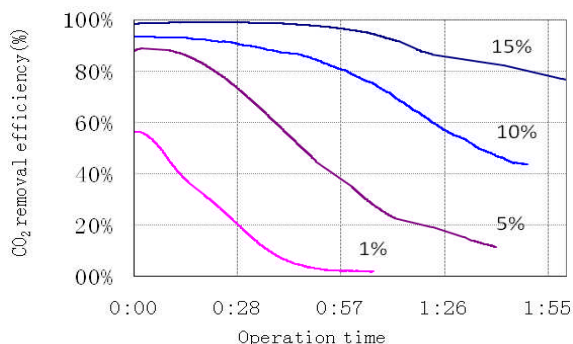


Fig.4. Removal efficiency lines in different concentration of aqueous ammonia in the semi-batch reactor

A semi-batch reactor as the above-mentioned has been used in this paper, 1%,5%,10%and15% concentrations of aqueous ammonia has been compared for the removal efficiency, shows in fig.4. The initial removal efficiency and the duration of above 80% removal efficiency in the same reaction conditions shows in fig.5-6. The experimental conditions were as following : temperature: 20.0°C (room temperature), pressure: 1atm, gas flow: 540 ml / min; and CO₂ concentration: 15%.

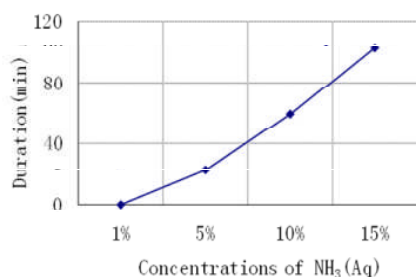


Fig.5. The duration of above 80% removal efficiency

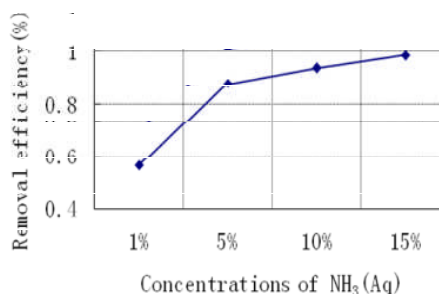


Fig.6. The initial removal efficiency

4.2 CO₂ absorption rate

A number of experiments have been done on different temperatures, concentrations of ammonia and CO₂ to test the carbon dioxide absorption with aqueous ammonia in the WWC, and some of the data shows in Table1-3:

Table.1. Absorption of CO₂ in 10%NH₃(aq), Total pressure:1.4-1.7 Bar, Liquid flow rate:2-3 cm³/s

T(K)	CO ₂ (g) Set Inlet Concentration	P _{CO₂,IN} (kPa)	P _{CO₂,OUT} (kPa)	P _{CO₂,b} (kPa)	Flux×10 ⁷ (mol/cm ² ·s)	K _G ×10 ¹⁰ (mol/pa·cm ² ·s)
293	5%	7.84	6.58	7.19	7.59	1.054
293	10%	16.64	14.12	15.35	15.01	0.978
293	15%	23.39	20.17	21.74	21.11	0.971
293	20%	31.84	27.04	29.37	32.40	1.103
313	5%	7.74	5.84	6.75	11.76	1.743
313	10%	15.4	11.93	13.61	22.38	1.644
313	15%	22.83	18.27	20.46	30.83	1.507
313	20%	31.31	24.8	27.92	44.87	1.607

Table.2. Absorption of CO₂ at 293K, Gas flow rate: 5SLPM/min, Total pressure:1.4-1.7 Bar, Liquid flow rate:2-3 cm³/s

NH ₃ (Aq) concentration	CO ₂ (g) Set Inlet Concentration	P _{CO₂,IN} (kPa)	P _{CO₂,OUT} (kPa)	P _{CO₂,b} (kPa)	Flux×10 ⁷ (mol/cm ² ·s)	K _G ×10 ¹⁰ (mol/pa·cm ² ·s)
1%	10%	15.32	14.74	15.03	3.66	0.243
5%	5%	7.55	6.75	7.14	4.78	0.669
5%	10%	15.82	14.18	14.98	10.47	0.698
5%	15%	26.27	23.84	25.04	14.32	0.572
10%	5%	7.84	6.58	7.19	7.59	1.054
10%	10%	16.64	14.12	15.35	15.01	0.978
10%	15%	23.39	20.17	21.74	21.11	0.971
10%	20%	31.84	27.04	29.37	32.40	1.103
15%	10%	16.85	13.27	14.99	20.86	1.392

Table. 3 Absorption of CO₂, CO₂:10%(set),Gas flow rate: 5SLPM/min, Total pressure:1.4-1.7 Bar, Liquid flow rate:2-3 cm³/s

T(K)	NH ₃ (aq) concentration	P _{CO₂,IN} (kPa)	P _{CO₂,OUT} (kPa)	P _{CO₂,b} (kPa)	Flux×10 ⁷ (mol/cm ² ·s)	K _G ×10 ¹⁰ (mol/pa·cm ² ·s)
293	1%	15.32	14.74	15.03	3.66	0.243
293	5%	15.82	14.18	14.98	10.47	0.698
293	10%	16.64	14.12	15.35	15.01	0.978
293	15%	16.85	13.27	14.99	20.86	1.392
313	1%	15.39	14.59	14.98	5.26	0.351
313	5%	15.41	12.83	14.08	16.77	1.191
313	10%	15.40	11.93	13.61	22.38	1.644

5. Result and discussion

5.1 Removal efficiency in aqueous ammonia

As shown in Fig.4, absorption capacity can be compared among different concentrations of ammonia. Fig.5 shows that the initial removal efficiency can reach 90% when the concentration of ammonia is higher than 5%, and the initial removal efficiency increases gradually with the increased concentration of ammonia. As the absorbent, how long can it have a high and stability removal efficiency is to be concerned as an important parameter. And Fig.5 shows the time that the removal efficiency is more than 80% in different concentration of solutions.

Phenomenon of the experiments shows that if the concentration of the aqueous ammonia is more than 15%, a lot of ammonia will volatilize from the solution, and low concentration of ammonia can also have higher rates of removal. Therefore, the concentration of aqueous ammonia should be selected from 5% to 10%.

5.2 Absorption rate and mass transfer in WWC

For the Hatta number $Ha > 2$ [16] (Versteeg and van Swaaij, 1988), the specific rate becomes:

$$N_{CO_2} = [CO_2]_i \sqrt{D_{CO_2} k_{OV}} = \frac{P_{CO_2}}{H_{CO_2}} \sqrt{D_{CO_2} k_{OV}} \quad (16)$$

N is the same as Flux in all the formulas. The Flux of CO₂ into or out of the solution can be characterized by mass transfer coefficients such as the overall gas transfer coefficient.

$$N_{CO_2} = K_G P_{CO_2,b} \quad (17)$$

The overall mass transfer coefficient, K_G , is calculated as the slope of the flux versus the log mean pressure [17].

$$P_{CO_2,b} = \frac{P_{CO_2,in} - P_{CO_2,out}}{\ln(P_{CO_2,in} / P_{CO_2,out})} \quad (18)$$

So the overall gas transfer coefficient K_G can be calculated by the Flux and $P_{CO_2,in}$ and $P_{CO_2,out}$. At the same temperature and concentration of ammonia, the value of K_G is fixed and can be calculated by the Flux- CO₂ partial pressure line. The K_G lines at 293K in 5%, 10% NH₃(aq) and 313K in 10% NH₃(aq) shows in Fig. 8. The lines used to calculate and compare the value of K_G ,

at different temperatures and concentrations of aqueous ammonia. The influence of aqueous ammonia concentration to K_G shows in Fig.9.

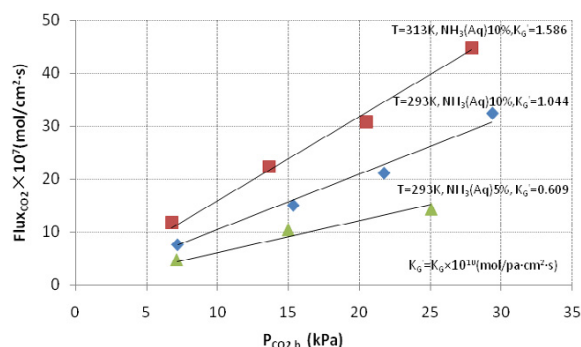


Fig.8. K_G calculated by Flux- CO_2 partial pressure lines

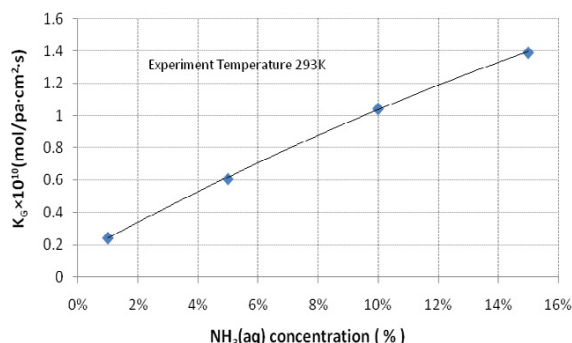


Fig.9. K_G - $\text{NH}_3(\text{aq})$ concentration curve at 293K

Fig.8 shows that K_G curves have a very good linearity, that indicates it is appropriate to use K_G in the mass transfer process of the carbon dioxide absorbed by aqueous ammonia. As shown in Fig.8 and Fig.9, with the temperature and the concentration of ammonia increased, the mass transfer coefficient K_G also increased, which is consistent with the basic principles of the reaction.

However, the curves and the law of K_G changing with different temperatures and ammonia concentrations need to be got by further experiments. The mass transfer model and the measurement of some basic mass transfer and kinetic parameters such as H , D , and k_{ov} etc. need further research.

Compared with the 0.6M PZ, plus 4M MDEA solution at low loading as 0.095 mol CO_2 /mol Amine^[18] (Bishnoi, 2000), 10% NH_3 (5.8M), have a higher Flux at the same temperature of 313K, that shows in Table4.

Table 4 Flux comparison between $\text{NH}_3(\text{aq})$ and MDEA+PZ

Temperature (K)	Absorbent	$P_{\text{CO}_2,b}$ (kPa)	$\text{Flux}_{\text{CO}_2} \times 10^7$ (mol/cm ² · s)
313	10% NH_3 (5.8M)	6.75	11.76
313	MDEA(4M)+PZ(0.6M) ^[18]	5.25	3.61

It can be observed clearly that the ammonia Flux is three times higher than MDEA + PZ under the same conditions. And further research of aqueous ammonia as CO_2 absorbent seems to be possible and necessary.

6. Conclusions

For 5% or higher concentration of ammonia, the initial removal efficiency of CO_2 can reach 90%. This shows that low concentration of ammonia can also have a higher rate of removal. Phenomenon of the experiments shows that if the concentration of the aqueous ammonia is more than 15%, a lot of ammonia will volatilize from the solution. Therefore, the concentration of aqueous ammonia should be selected from 5% to 10%. Aqueous ammonia has a high Flux in WWC, which is three times higher than that of MDEA+ PZ, under the same conditions.

K_G curves got in WWC have a very good linearity, that indicates it is appropriate to use K_G in the mass transfer process of the carbon dioxide absorption by aqueous ammonia. However, the curves and the law of K_G changing with different temperatures and ammonia concentrations need to be got by further experiments. The mass transfer model and the measurement of some basic mass transfer and kinetic parameters such as H_{CO_2} , D_{CO_2} , and k_{ov} in aqueous ammonia et al need further experiments to study. The paper shows that aqueous ammonia is promising as an absorbent for CO_2 removal and needs to be further studied.

Notation

D	diffusion coefficient, m ² /s
H	Henry's law constant, m ³ Pa/kmol
N_X	Flux of species x, kmol/m ² s
P_X	partial pressure of x, Pa
T	temperature, K
K_G	overall gas transfer coefficient, mol/pa.cm ² · s

K_{OV} overall pseudo-first-order reaction rate constant, S^{-1}
 Ha Hatta number

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